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Thermodynamic characteristics of sorption of metal-ions by ion exchangers

Conditions of sorption equilibrium of copper, zinc, cadmium and lead-ions by chelatforming resins Diaion CR 11, Dowex M 4195 and Duolite C 467 depending on the degree of neutralization of their ionogenic groups, the acidity of the medium and concentration of solutions are studied; corresponding equations expressing the isotherms of sorption are offered. Kinetics of these processes is studied; on the basis of equilibrium and kinetic parameters are calculated thermodynamic quantities. It is shown that under selected conditions the selectivity is controlled by enthalpy factor with calorification and a decrease in entropy.

Keywords: *ion exchanger resins; sorption isotherms; isotherm equations; kinetic and thermodynamic quantities.*

Introduction

The availability of data on the equilibrium of ion exchange is necessary for selection and optimization of the conditions of ion concentration, ejection of a concrete ion from a complex system and for its separation from the other ions, as well as for the calculation and designing of technological equipment. As a result the investigation of equilibrium conditions of ion exchange brings to deriving of isotherm equations and to determination of the exchange constant and coefficient of selectivity. For this reason, the study of model solutions in the way of increase of sorption selectivity is regarded as an actual problem. The aim of the present research work is to study the mutual influence of ion exchangers under consideration and ions of non-ferrous metals for the comparative evaluation of their sorption capacity.

Studies are carried out at the follows chelatforming resins: macroporous Duolite C 467 with aminophosphonic functional group, macroporous Dowex M 4195 with bis-piccolilamine functional group and highporous Diaion CR-1 with iminodiacetic acid functional group [1].

Experimental Section

As the deprotonated form for the chelatforming resins is coordinating-active their industrial form (Diaion CR 11 and Duolite C 467 $-\text{Na}^+$, Dowex M 4195 $-\text{SO}_4^{2-}$) was used; processes were carried out at the static conditions, in the ratio of resin:solution = 1:100. Concentration of the residual

after sorption of the studied ions from the solution is determined by complexometric method using pyridile-azo-naphthol PAN (Cu^{2+}), eriochrome black T (Zn^{2+} and Cd^{2+}) and xylenole orange (Pb^{2+}) [2]. At the joint presence of studied ions their content in the solution was determined by AAS method on the spectrometer Thermo Scientific iCE 3500 AA. The quantity of ions absorbed by the resins is found on the basis of difference between the beginning and after sorption concentration. Kinetics of these processes is studied by the method of "limited capacity" with solutions of initial concentration 1,0 g Me/l; the values of effective diffusion coefficients are calculated from the equation offered by G. Boyd and colleagues [3].

Results and Discussion

Diaion CR 11, Duolite C 467 and Dowex M 4195 are characterized by the functional groups of $-\text{N}(\text{CH}_2\text{COONa})_2$, $-\text{NH}-\text{CH}_2-\text{PO}(\text{ONa})_2$ and $\text{C}_5\text{H}_4\text{N}-\text{CH}_2-\text{N}-$ (matrix) $-\text{CH}_2-\text{C}_5\text{H}_4\text{N}(\text{SO}_4^{2-})$ respectively; the sorption by the first 2 polyampholytes is realized at the expense of replacement of Na^+ ions with Me^{2+} ions and coordinating bond between the N atoms and Me^{2+} ions, the sorption of Me^{2+} ions by Dowex M 4195 is carried out at the expense of formation of matching complexes. Production of chelate acids in the resin phase, in other words, the selectivity of ion exchangers depends basically on the chemical nature of their functional groups and conditions of the sorption process conducting; kinetic parameters of sorbents, regeneration liability, swelling rates, mechanical and thermal stability depends on the properties of a polymer matrix [4], in this connection these factors are also evaluated. Because of the fact that the groups of polyampholytes with the base nature depending on the medium acidity are subjected to partially or completely dissociation they are responsible for the sorption of metal ions at the expense of co-ordination bond. The sorption capacity of polyampholytes determines the quantity of acid groups, and the selectivity of sorption processes – basicity of amine groups and stereochemistry of ligand groups. Under small values of pH the acid groups of resins are weakly dissociated, that is why occurs the competitive sorption for functional groups between hydrogen and metal ions. In addition, effective mutual influence between ions and functional groups of the resins cannot realize because of protonation of amine groups.

Sorption isotherms for all studied systems are made (fig. 1); parameters included in the considered models (Langmuir, Freundlich, Sips and Redlich–Peterson) are calculated on the basis of values get during the experiment. Analysis of the experimental data confirms with certain deviations the possibility of expression of the studied processes by the Langmuir equation with sufficient precision. This fact shows that there is a layer of monomolecular sorption in these systems and all sorption centers are characterized by equal energy. Freundlich equation can describe only beginning parts of the sorption curves: (0,25–1,50 gMe/l).

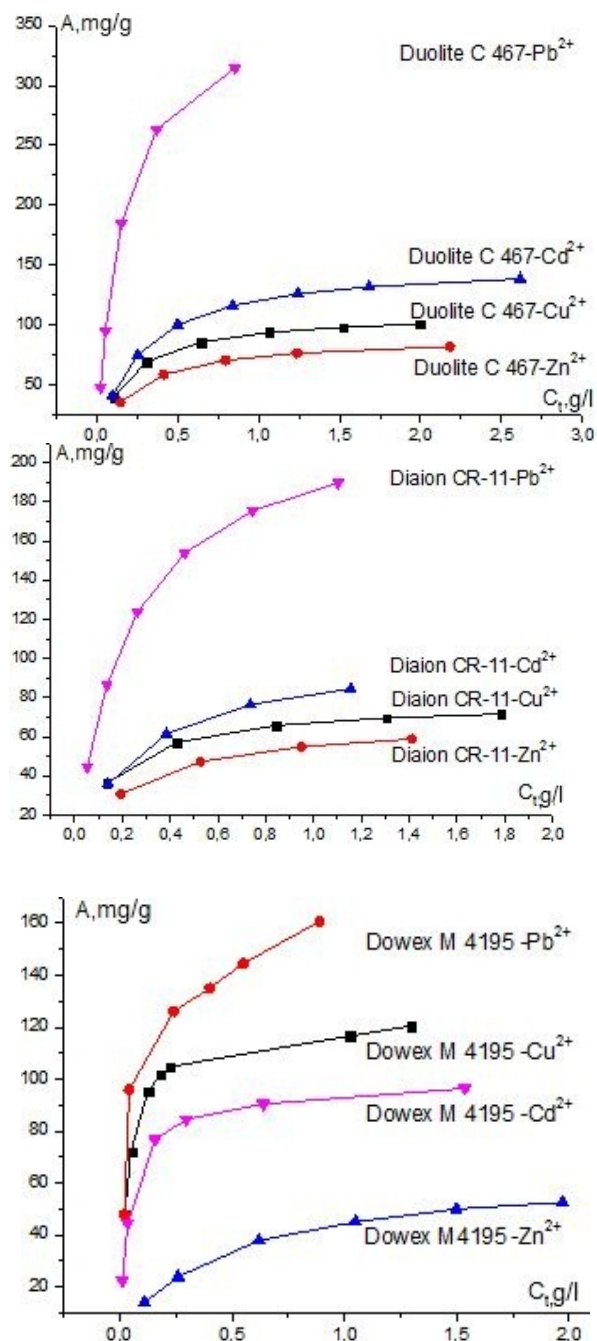


Fig. 1. Isotherms of sorption of Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} -ions by studied resins

The deviations in saturation regions of the curves between values theoretically calculated and the experimental results are so great that it becomes meaningless to compare. Three unknown parameters are included to the equations of Sips ($A = K_s \cdot C_t^{1/n} / 1 + \alpha_s \cdot C_t^{1/n}$) and Redlich-Peterson ($A = K_{RP} \cdot C_t / 1 + \alpha_{RP} \cdot C_t^\beta$) [5]; therefore the minimization procedure is used [6], results adequately satisfying theoretical and practical data aren't obtained. In our opinion, the cause of it is concerned with the fact that last two models have been simulated on the basis of the hybrid mechanism. For Duolite C 467: $Pb > Cu > Zn > Cd$, for Diaion CR 11: $Cu > Pb > Zn > Cd$ and for Dowex M 4195: $Cu > Pb > Zn > Cd$ selectivity sequences are determined; it is revealed that the polyampholyte with aminophosphon group is the most effective sorbent for the studied ions. All isotherms made by the method of changing concentrations are noted for the relief depending on the selectivity of the resin against the concrete ion. Absence of curves in the isotherms allows to suppose that absorption occurs mainly at the expense of functional groups. a and n included in the Freundlich equation are found from the graphic $-\lg x/m = a \cdot C_t^n$. At the specified graphic dependence the length of the segment cut from the ordinate axes gives the value of a , tangent of the angle formed by a straight line with the abscissa axis gives the value of n . In the foregoing sequence the forms of isotherms corresponding to Langmuir and Freundlich equations are the follows:

Duolite C 467	$Pb^{2+}: A = 370,6 \cdot (6,65 \pm 0,06) \cdot C_t / 1 + (6,65 \pm 0,06) \cdot C_t$	$A = 660,7 \cdot C_t^{0,7}$
	$Cu^{2+}: A = 109,6 \cdot (5,60 \pm 0,05) \cdot C_t / 1 + (5,60 \pm 0,05) \cdot C_t$	$A = 95,5 \cdot C_t^{0,27}$
	$Zn^{2+}: A = 90,2 \cdot (4,51 \pm 0,04) \cdot C_t / 1 + (4,51 \pm 0,04) \cdot C_t$	$A = 81,3 \cdot C_t^{0,62}$
	$Cd^{2+}: A = 152 \cdot (3,87 \pm 0,04) \cdot C_t / 1 + (3,87 \pm 0,04) \cdot C_t$	$A = 125,9 \cdot C_t^{0,37}$
Diaion CR 11	$Cu^{2+}: A = 77,8 \cdot (6,46 \pm 0,03) \cdot C_t / 1 + (6,46 \pm 0,03) \cdot C_t$	$A = 74,13 \cdot C_t^{0,38}$
	$Pb^{2+}: A = 227,9 \cdot (4,50 \pm 0,04) \cdot C_t / 1 + (4,50 \pm 0,04) \cdot C_t$	$A = 234,4 \cdot C_t^{0,55}$
	$Zn^{2+}: A = 68,7 \cdot (4,19 \pm 0,04) \cdot C_t / 1 + (4,19 \pm 0,04) \cdot C_t$	$A = 57,74 \cdot C_t^{0,36}$
	$Cd^{2+}: A = 104 \cdot (3,75 \pm 0,06) \cdot C_t / 1 + (3,75 \pm 0,06) \cdot C_t$	$A = 93,3 \cdot C_t^{0,44}$
Dowex M 4195	$Cu^{2+}: A = 120,4 \cdot (29,5 \pm 0,05) \cdot C_t / 1 + (29,5 \pm 0,05) \cdot C_t$	$A = 325,6 \cdot C_t^{0,75}$
	$Zn^{2+}: A = 52,55 \cdot (3,95 \pm 0,06) \cdot C_t / 1 + (3,95 \pm 0,06) \cdot C_t$	$A = 50,12 \cdot C_t^{0,59}$
	$Pb^{2+}: A = 160,65 \cdot (21,1 \pm 0,5) \cdot C_t / 1 + (21,1 \pm 0,5) \cdot C_t$	$A = 245,5 \cdot C_t^{0,70}$
	$Cd^{2+}: A = 96,40 \cdot (24,4 \pm 0,4) \cdot C_t / 1 + (24,4 \pm 0,4) \cdot C_t$	$A = 83,2 \cdot C_t^{0,34}$

The study of kinetics of these processes shows in all cases that the sorption equilibrium arises in 2.5–3 hours. Simple and reliable method of “kinetic memory”, in other words, the partition method, is used for the experimental determination of demarcation stage. The increase in sorption rate in all cases after partitioning in comparison with the initial rate confirms that processes under the control of pore diffusion. The dependence of $-\lg(1-F)$ on time isn't expressed by a straight line under low saturation degrees, under higher saturation values ($F > 0.5-0.6$) dependence are expressed by a straight line. The expression of saturation degree up to the values of dependence F -in $t^{1/2}$ equal to 0.4–0.5 by the straight line

going from the beginning of origin of coordinates and quantities calculated for the prices charged for absolute values of the Bio criterion ($Bi > 50$) confirm once again that the processes are under control of the pore diffusion. The sorption rates of ions by the polyampholytes at the different way with increase in temperature. The positive effect of the temperature on the rate of processes is observed more clearly during the sorption of cadmium and lead ions: no matter how great are the values calculated for the activation energy, more intensive changes simultaneously with the change of the temperature the sorption rate. This is also evident in the 2nd figure. The values received by us for the activation energies are characteristic for sorption processes realized in the region of the pore diffusion.

Kinetic and thermodynamic parameters of studied systems

$D_i \cdot 10^{-7}$, Cm ² /sec	$D_0 \cdot 10^{-3}$, Cm ² /sec	$E_{akt.}$, kCal/ mol	$-\Delta S^0$, C/ mol.K	$-\Delta H^0$, kCal/mol	$-\Delta G^0$, kCal/mol	K	$\lambda^2 e^{AS/R} \cdot 10^{-17}$, Cm ²
Duolite C 467-Pb ²⁺							
0,85	0,197	13,50	44,64	17,86	4,55	6,29	1,169
Duolite C 467-Cu ²⁺							
0,70	0,616	16,80	73,44	25,24	3,36	3,88	0,0365
Duolite C 467-Zn ²⁺							
0,64	0,012	18,50	68,48	22,82	2,41	2,65	0,006
Duolite C 467-Cd ²⁺							
0,45	0,0275	21,60	61,00	20,81	2,64	2,90	0,0246
Dowex M 4195-Cu ²⁺							
0,28	0,049	18,50	56,21	27,48	10,73	75,94	0,29
Dowex M 4195-Zn ²⁺							
0,16	0,7068	26,50	34,00	11,25	1,12	1,57	4,18
Dowex M 4195-Pb ²⁺							
0,145	0,959	27,50	31,47	18,13	8,75	34,26	5,68
Dowex M 4195-Cd ²⁺							
0,12	4,88	32,00	17,95	7,07	1,72	2,0	28,88
Diaion CR-11-Cu ²⁺							
0,75	0,087	17,50	51,375	18,55	3,24	3,70	0,518
Diaion CR-11-Pb ²⁺							
0,55	0,2156	20,50	43,88	16,43	3,36	3,88	1,276
Diaion CR-11-Zn ²⁺							
0,40	0,35	22,5	39,86	13,57	1,69	1,98	0,078
Diaion CR-11-Cd ²⁺							
0,35	0,844	25,0	32,54	11,77	2,074	2,31	0,005

Thermodynamical parameters of sorption of the studied ions by the polyampholytes are calculated on assumption of ideal conditions for the ionite phase, in other words, without taking into account the factor of activity of sorbed ions at the ionite phase. In all cases, the sorption of ions is accompanied with calorification ($\Delta H < 0$). The connection between the increase in sorption selectivity and decrease in entropy determined by us is justified in all investigated systems. A case of more rapidly establishment of the sorption equilibrium is specific for small values of the entropy factor. The values of the entropy factor are calculated in compliance with [7].

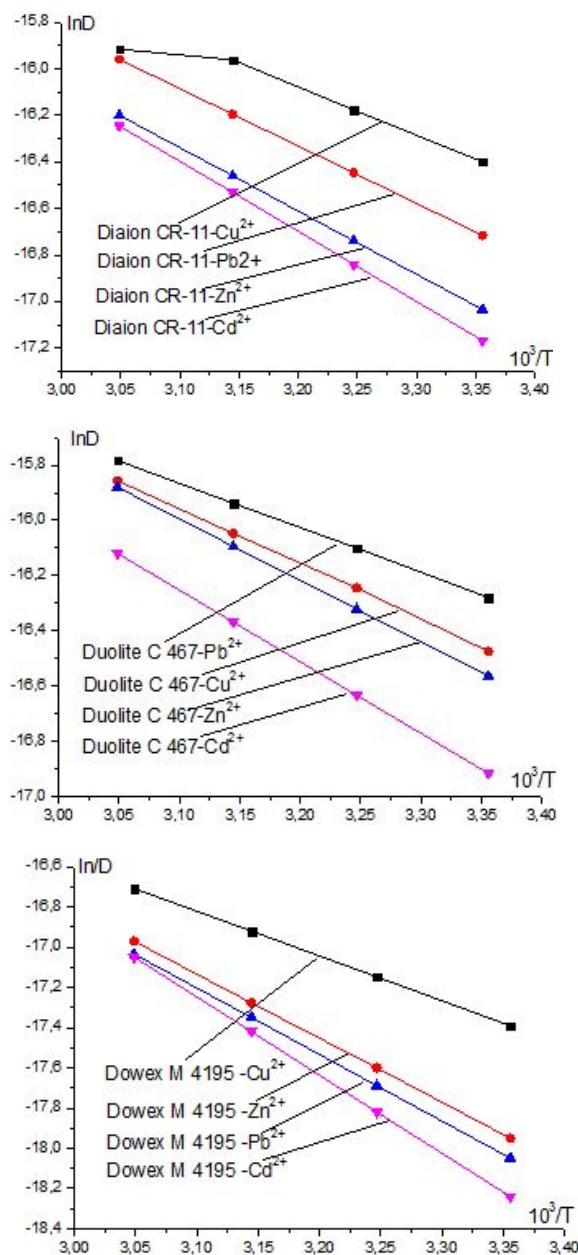


Fig. 2. The dependence of the sorption of the studied ions ion exchangers Diaion CR 11, Duolite C 467 and Dowex M 4195 on the temperature

Characterization of the entropy factor of Duolite C467 by smaller values, the rapid establishment of sorption equilibrium is connected with the fact that its matrix is macroporous and it has to a certain extent relatively large sorption capacity.

The results obtained confirm the fact that the thermodynamic parameters of sorption processes carried out at high speed and selectivity are characterized by minimum values. According to calorification and decrease in entropy it is possible to suppose that in all systems investigated by us the selectivity is controlled by the enthalpy factor. As can be seen from the table, the polyampholites can be arranged in the follows order according to their kinetic indexes: Duolite C 467>Diaion CR 11>Dowex M 4195. The kinetic parameters of the highporous Diaion CR 11 expressed by relative low values in comparison with the macroporous Duolite C 467 must be explained, in our opinion, by its small exchange capacity. The values of half-time of exchange calculated for all system confirm these comments. The values of time of half-exchange for copper ion by the ionites Duolite C 467, Diaion CR 11 and Dowex M 4195 are respectively the following: 425 sec, 397 sec, 1063 sec.

Conclusions

The maximum degree of extraction of copper ions studied sorbents is about 90–95% of the injected amount (0,5–1,0g/l). Quantitative separation of two ions mixture by the method of selective sorption is achieved if distribution coefficients of sorbed and non-sorbed ions have the following order: $P_1 > 100-300$ and $P_2 < 3-10$ and their ratio is 10–30 [8]. When combined presence of copper and zinc with Dowex M 4195, lead and zinc ion exchangers Duolite C 467 and Diaion CR 11 in the range of pH 4.5–5.5 ratio P_1/P_2 to be about 10–30. At these sorbents, under certain conditions it is possible to conduct a quantitative separation of ions copper and lead from zinc and some degree of cadmium. Good sorption of ions copper and lead indicates the selectivity of ion exchangers for the studied ions copper and lead. By sorption of binary solutions of copper and zinc with an initial concentration of 0,5 g/l ($0,25 \text{ gCu}^{2+}/\text{l} + 0,25\text{gZn}^{2+}/\text{l}$) ion exchanger Dowex M 4195, lead and zinc ($0.25 \text{ g Pb}^{2+}/\text{l} + 0.25 \text{ gZn}^{2+}/\text{l}$) ion exchangers Duolite C 467 and Diaion CR 11 for the partition coefficient obtained respectively the following values: 30.30, 24.86 and 20.36. As can be seen, with the joint presence of these ions corresponding ion exchangers division proceeds efficiently. The data show that of industrial wastewater and other similar objects with a concentration of 0,5 g / l of copper and lead, they can be cleaned studied ion exchangers.

References

1. Chromatography. Products for analysis and purification. Supelco. Sigma-Aldrich Chemie GmbH. 2003/2004. P. 453 (Catalogue).
2. Shvartsenbach G., Flashka G. Complexonometric titration. Moscow : Chemistry, 1970. 562 p. (in Russian) (Book with editor).
3. Boyd G.E., Adamson A.W., Myers L.S. The exchange adsorption of ions from aqueous solutions by organic zeolites.II. Kinetics // J. Am. Chem. Soc. 1947. Vol. 69, No. 11. P. 2836–2848 (Journal article).
4. Khering R. Chelatforming ionexchangers. Moscow : World, 1971. 279 p. (in Russian) (Book with editor).

5. Allen S.J., Gan Q., Matthews R., Jhonson P.A. Comprasion of optimised isotherm models for basic dye adsorption by kudzu // *Bioresource Technology*. 2003. Vol. 88, No. 2. P. 143–152 (Journal article).
6. Redlich O., Peterson D.L. A useful absorption isotherm // *J. Phys. Chem.* 1959. Vol. 63, No. 6. P. 1024–1026 (Journal article).
7. Glasstone S., Laidler K., Eyring H. *The Theory of Rate Processes*. N.Y. ; London : Princeton University, 1941. 501 p. (Book with editor).
8. Marchol M. İonexchangers in analytical chemistry. The property and application in inorganic chemistry. Moscow : World. 1985. Vol. 1. 264 p. (in Russian) (Book with editor).

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